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Review on advanced of solar assisted chemical heat pump dryer for agriculture produce

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ABSTRACT

Over the past three decades there has been nearly exponential growth in drying R&D on a global scale. Improving of the drying operation to save energy, improve product quality as well as reduce environmental effect remained as the main objectives of any development of drying system. A solar assisted chemical heat pump dryer is a new solar drying system, which have contributed to better cost-effectiveness and better quality dried products as well as saving energy. A solar collector is adapted to provide thermal energy in a reactor so a chemical reaction can take place. This reduces the dependency of the drying technology on fossil energy for heating. In this paper a review on advanced of solar assisted chemical heat pump dryer is presented (the system model and the results from experimental studies on the system performance are discussed). The review of heat pump dryers and solar assisted heat pump dryer is presented. Description of chemical heat pump types and the overview of chemical heat pump dryer are discussed. The combination of chemical heat pump and solar technology gives extra efficiency in utilizing energy.

Contents

1. Introduction

Sun drying is the common method used to preserve agricultural products in tropical and sub-tropical countries [1]. However, this process has many disadvantages: spoilt products due to rain, wind, moisture and dust; loss of produce due to birds and animals; deterioration in the harvested crops due to decomposition, insect attacks and fungi, etc. Further, the process is labor intensive, time consuming and requires a large area for spreading the produce out to dry. Solar-drying technology offers an alternative which can process the vegetables and fruits in clean, hygienic and sanitary conditions to national and international standards with zero energy costs. It saves energy, time, occupies less area, improves product quality, makes the process more efficient and protects the environment [2].

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Nomenclature

A_c	collector area (m^2)
A_s	exposed area of storage tank (m^2)
COA	efficiency heating of chemical heat pump
COP^h	coefficient of performance of chemical heat pump
G	gas
I	solar radiation (MJ/m^2)
P	pressure (bar)
Pc	condenser pressure (bar)
Pe	evaporator pressure (bar)
Q_c	condenser heat rejection (kJ)
Q_r	reaction heat (kJ)
Q_s	storage tank heat loss (kJ)
Q_u	useful energy gain of collector (W)
S	metallic salt
SF	solar fraction
Ta	ambient air temperature (K)
Tc	condenser temperature (K)
T_l	liquid storage tank temperature (K)
Te	evaporator temperature (K)
Tg	reactor temperature at regeneration stage (K)
Tm	mean collector temperature (K)
ΔH_c	enthalpy of condensing (J/mol)
ΔH_r	enthalpy of chemical reaction (J/mol)
ΔS	change of entropy (K)
$(UA)_{str}$	storage tank loss coefficient (W/K)
η	collector efficiency
η_{eva}	evacuated tube collector efficiency

Kiebling [3] has listed 66 different solar dryers, their configurations, capacity, products dried and cost. Fuller [4], and Ekechukwu and Norton [5] have reviewed many solar dryers, and compared their performance and applicability in rural areas. Sharma [2] has presented a comprehensive review of the various designs, details of construction and operational principles of the wide variety of practically realized designs of solar-energy drying systems and a systematic approach for the classification of solar-energy dryers has been evolved. A review of new technologies, models and experimental investigations of solar driers has been presented by Ramana [6], popular types of driers in Asia-Pacific region, and new types of driers with improved technologies have been discussed. A comprehensive procedure for performance evaluation of solar food dryers has been presented by Augustus et al. [7], a detailed review of parameters generally used in testing and evaluation of different types of solar food dryers has been presented.

Most solar dryers developed are designed for specific products or class of products. Vegetables such as chilli, cassava, onion, radish, ginger, peas, corn, mushroom, tamarind and coconut, and fruits such as mango, apple, pineapple, banana, grapes, prunes and longans [8,9]. Selection of a solar dryer for a particular food product is determined by quality requirements, product characteristics and economic factors. A systematic classification of available solar food dryers, based on the design of system components and the mode of utilization of solar energy, is presented in Fig. 1 [7].

Solar-assisted dryers are conventional dryers to which supplementary equipment is added to enable a significant proportion of the thermal energy required for drying to be replaced by solar energy. In these types of dryer, a planned, and generally optimized drying process can be achieved to obtain superior product quality and good economic performance. Any influence of the weather conditions on product quality and on the performance of the dryer can be eliminated by using an independent energy source, if needed, and proper control facilities [10]. The construction of the solar

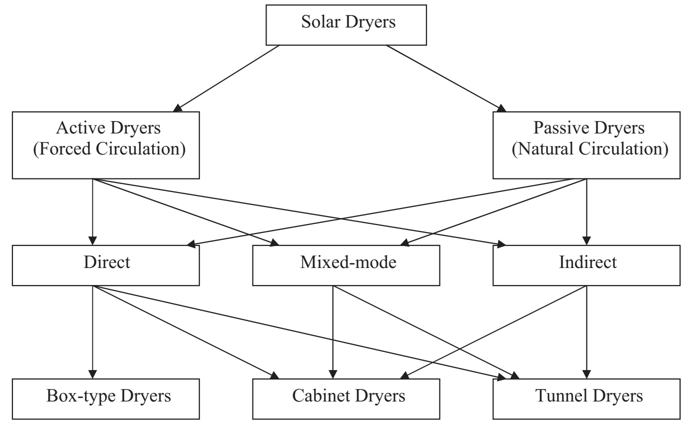


Fig. 1. Classification of solar dryers and drying modes [7].

assisted dryers is relatively complex compared to other dryers. They usually consist of a solar collector, a fan, a heat storage system, a burner/heater, and a control system. They can handle large quantities and deliver good product quality [11]. The application of heat storage in solar drying system is justified by three circumstances: (i) drying period can be extended by the stored energy, (ii) the surplus energy appearing at the radiation peaks can be stored to avoid local overdrying, (iii) the temperature of the drying air can be controlled to avoid damage to material [12].

The low temperature thermal requirement of the heat pump makes the system an excellent match for thermal applications for both domestic and industrial use; such as water heating, solar drying, space cooling, and space heating and cooling. Heat pump dryers have been known to be energy efficient when used in conjunction with drying operations. The principal advantages of heat pump dryer's energy from the ability of the Heat pumps to recover energy from the exhaust gas as well as their ability to control the drying gas temperature and humidity [13]. Different types of HPs are available on the market for drying applications. Neslihan and Arif [14] classified the HPD application under three main topics, air source heat-pump drying systems, ground source heat-pump drying systems, and chemical heat-pump drying systems.

A chemical heat pump (CHP) is proposed as one of the potentially significant technologies for effective energy utilization in drying. Ogura and Mujumdar [15] studied the CHP and proposed a chemical heat pump dryer (CHPD) system for ecologically friendly effective utilization of thermal energy in drying.

CHPs are those systems that utilize the reversible chemical reaction to change the temperature level of the thermal energy which stored by chemical substances [16]. These chemical substances play an important role in absorbing and releasing heat [17]. The advantages of thermochemical energy storage, such as high storage capacity, long term storage of both reactants and products, lower of heat loss, suggests that CHP could be an option for energy upgrading of low temperature heat as well as storage [18].

In this paper the authors proposed a new approach of solar assisted dryer namely solar assisted chemical heat pump dryer (SACHPD). The review of heat pump dryers and solar assisted heat pump dryer is presented. Description of chemical heat pump types and the overview of chemical heat pump dryer are discussed, and the review on advanced of the (SACHPD) for agriculture produce is presented.

2. Heat pump dryers and solar assisted heat pump dryers

2.1. Heat pump dryers

Drying is an energy-intensive process and, in order to make the system energy efficient, it is necessary to have a better understand-

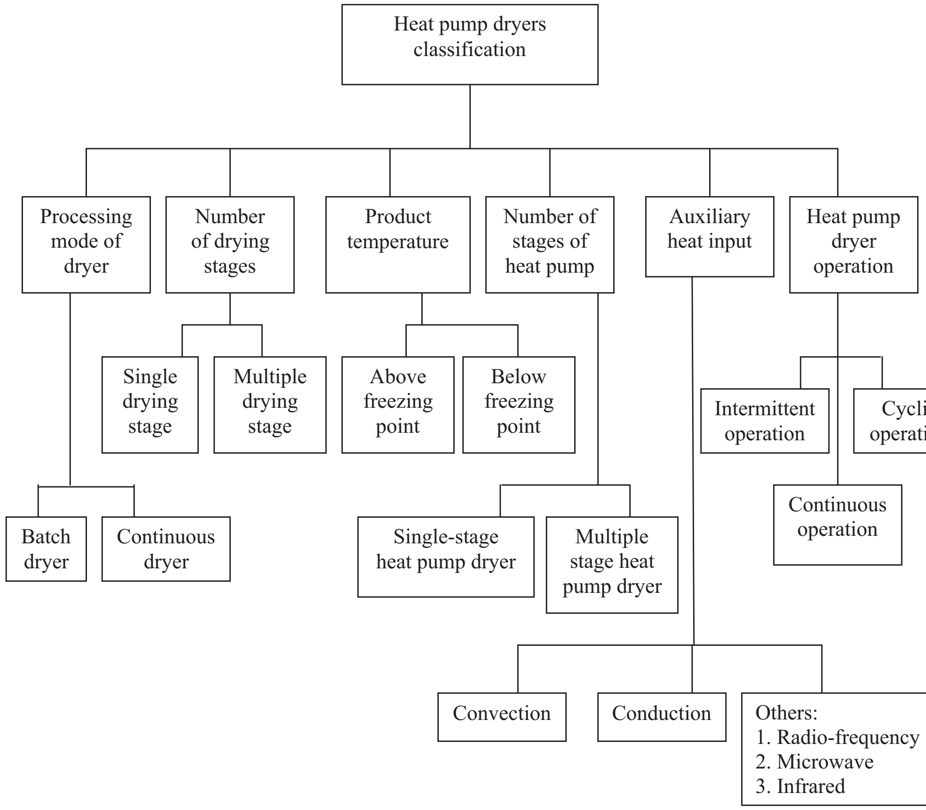


Fig. 2. A generalized classification scheme for heat pump dryers [13].

ing of the problem. In conventional dryers, humid air from the dryer is vented to the atmosphere, which results in the loss of both sensible and latent heat of vaporization of its moisture content. This energy can be recovered with the use of a heat-pump dryer. The humid air at the exit of the dryer is allowed to pass through an evaporator, where sensible and latent heat of the air can be recovered. This heat is transferred to the condenser for heating of the air before it enters the dryer [19]. Heat pumps have been extensively used by industry for many years, although their application to process drying and, in particular, to drying textile products is relatively lower [20].

The first HPD patent applications were started in 1973 and the first HP drying studies in the literature were done by Hodgett [21] and Geeraert [22]. Hodgett [21] reported that; energy consumption of HPD was less than conventional steam heated dryer, while Geeraert [22] studied on HP timber drying. Tai et al. [23] presented advantages of HPD systems and Oliver [24] studied on dehumidifying HPs used extensively for timber drying. Zylla et al. [25] concluded that SMERs increased as the relative humidity of the dryer outlet air increased. Cunney and Williams [26] reported that a well designed engine driven HP could achieve a reduction of about 30–50% in drying energy cost. Newbert [27] showed that the energy consumption could be reduced by 40% for drying of malt with a coupled gas engine HP (GEHP) dryer. In 1988, about 7% of the industrial HPs were used for drying. These HPs represented an installed capacity of 60 MW [28]. In 1992, Meyer and Greyvenstein [29] analyzed the life cycle cost of HPD application for grain drying. Several patents have been granted for products and processes in the field, and several types of HPDs have been manufactured internationally [30]. In 2006, the optimum operating temperatures and the optimum sizes of system components were calculated at which minimum life cycle cost occurred for the HPD system by Soylemez [31].

In most of these studies, food products and agricultural materials were dried in various types of HPDs. Fig. 2 displays a generalized classification scheme for heat pump dryers based on the processing mode number of drying stages and number stages of heat pump, types of auxiliary heat input, and heat pump dryer operation [13].

2.2. Solar heat pump dryers

The solar assisted heat pump drying system operated successfully. The heat pump recirculation mode and solar mode can be used to produce the same quality of drying. This allows the drying process to be continues and to save energy by not burning fossil fuels [32]. Best el al. [32] used of a combined solar heat pump dryer system for rice drying and has been developed as an alternative to conventional mechanical dryers.

Hawlader and Jahangeer [33] built a fully equipped experimental solar assisted HP drying system set-up for drying of green beans. This system illustrated in Fig. 3 schematically.

A solar assisted heat pump drying system with an energy storage tank has been proposed by Xie et al. [34]. The drying system is designed such a way that some of the components can be isolated depending on the weather conditions and usage pattern. The performance of the whole system has been modeled and investigated under a typical summer day of the city Baoding, China.

A heat pump dryer using multifunctional solar thermal collector designed and studied at the National University of Malaysia (Universiti Kebangsaan Malaysia) [35]. This system consists of five main components: vapor compression heat pump system, multifunctional solar thermal collector, drying chamber, air duct and solar collector hot air channel (Fig. 4). The multifunctional solar thermal collector attached to the system used to maintain the power in the drying chamber and also to increase the system efficiency and consists of aluminium rods and fins to transfer heat to and from the air passing through it. The collector is covered by the transparent plas-

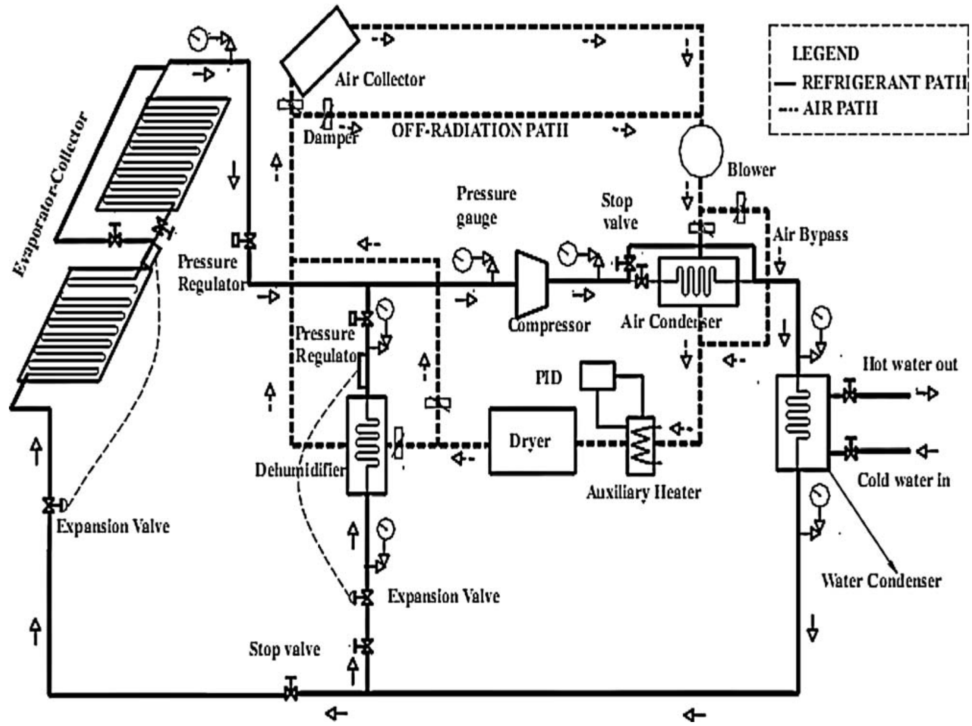


Fig. 3. Schematic of a solar assisted heat-pump drying system and water heater [33].

tic sheet on the top, and insulated by rubber foam on the bottom. The multifunctional collector is designed to operate as heat collector during sunshine hours and as evaporator during night hours or when solar radiation is insufficient. Therefore, it will increase the overall efficiency of the system and also extended the operation time [36–38].

3. Chemical heat pump (CHP)

The CHP can store thermal energy such as the waste heat from dryer exhaust, solar energy, geothermal energy, etc. in the form of chemical energy, and release the energy at various temperature levels during the heat-demand period.

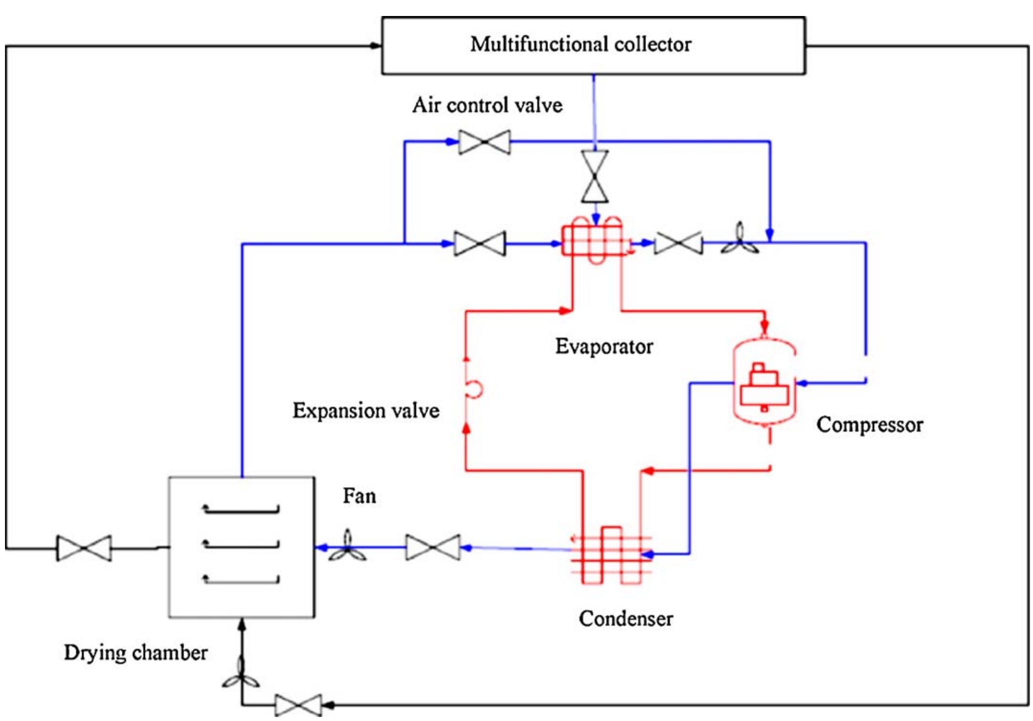


Fig. 4. Solar assisted heat pump drying using multifunctional solar collector-schematic diagram [36–38].

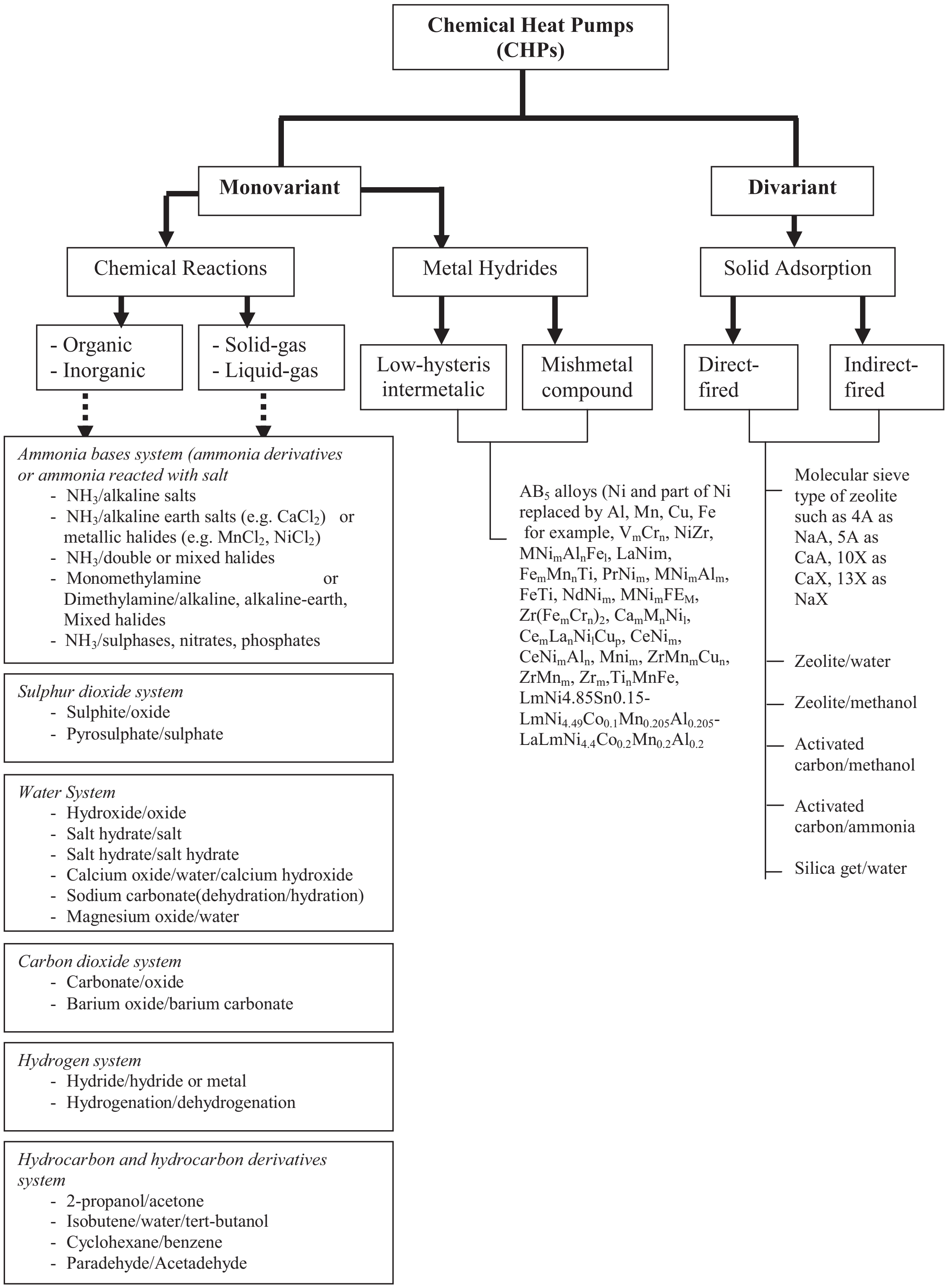


Fig. 5. Classification of CHP [39].

The general classification of CHP is shown in Fig. 5. Systems involving chemical reaction and requiring only one state variable (e.g. pressure) to be specified are mono variant systems, and these induce volume changes, while those that require both the temperature and pressure to be specified are di variant systems [39]. Various chemical substances have been used successfully in chemical heat pumps, such as water systems (hydroxide/oxide, zeolite/water; [40]), ammonia systems (salt/ammonia, amine complexes; [41], sulfur dioxide systems (sulfite oxide, pyro-sulfate/sulfate; [42]), hydrogen systems (hydrides, hydrogenation; [43]) and various others.

The working pairs are used for describing the technology status of the CHP [39]. Working pairs are used substances or chemicals without changing their properties; this is lead to consumption

or production of heat in endothermic/exothermic systems. The major requirements of working pairs, properties are their high storage capacity, thermal stability within the working conditions (temperature and pressure range), high thermal conductivity, high external heat transfer coefficient, high specific power output, transportability (easy to handle), small specific volume, non-corrosive and non-toxic (environmental friendly), low viscosity and surface tension, etc. [44]. Besides, ideal working pairs should also meet matching requirements for reaction temperature and rate, so as to improve system efficiency, to reduce equipment size and to shorten cycling time, etc. [45].

Lebrun and Neveu [46] suggest the following criteria be considered in the selection of an appropriate working pair: economic criteria (cost of working pair itself or cost of equipment), performance criteria (temperature rise, specific power production, mass of working pair), and cost and performance criteria (specific power per unit mass and unit area of exchange surface or temperature rise by unit mass or unit area of exchange surface). Neveu and Castaiang [47] note that the selection of working pairs needs the understanding of the machine's characteristics as a function of target temperature required. Neveu and Castaiang [47]; Orgaz and Dantzer [48]; and Sun [49] have discussed some methods on the selection of chlorides and metal alloys. The followings discuss a thermal–chemical method using Clapeyron diagram to make the selection of chlorides for different types of heat transformers. The method is based on the Van't Hoff expressions of solid–gas reaction equilibrium and the liquid–vapor equilibrium as well as some matching relations. From the main purpose of heat transformers, the principle for selection is to realize maximum temperature lift under permitted temperature and pressure limits.

Chemical heat pumps are normally classified into two types: solid–gas and liquid–gas. Solid–gas chemical heat pumps consist of reactor (s) (or adsorbers), evaporator (s) and condenser (s). Liquid–gas systems have at least two reactors: endothermic and exothermic reactors. Other auxiliary equipment is also normally required in these systems. The most critical component of CHPs is the reactor, where heat and mass transfer, chemical, adsorption and absorption occur. Many researchers have developed models to simulate the dynamic behavior of the reactor [50–55]. Stitou and Crozat [56] classify models into three categories: local, global and analytical models. The local model is to establish partial differential equations concerning heat transfer, mass transfer and dynamic mechanics on infinitesimals and to solve them by numerical methods; the global model is to consider the reactor's characteristic variables and average parameters in some groups of differential equations; the analytical model is to use average parameters during the reaction process as variables, so the differential equations are only related to space variables. It can be seen that their differences lie in the method of how to deal with variables as well as the form of equations. Goetz and Marty [50] and Lu et al. [57] have proposed grain–pellet model methods and shrinking-core model methods to solve these equations.

3.1. Liquid–gas CHP

In this type there are two reaction; exothermic (at higher temperature) and endothermic (at lower temperature). Exothermic reaction is given a useful heat but endothermic reaction is used a heat supply in lower temperature. The catalyst through the reactant is in the liquid phase. In a simple description for the reactant when the vapor release from endothermic reaction cause the backward reaction in another reactor, hence the Exothermic reaction takes place and temperature is upgrading [39].

Heat pumps based on acetone/hydrogen/2-propanol have been studied by many researchers [43,58–62]. Mathematical models to simulate the performance of this working pair have been developed [61]. Studies on a suitable catalyst have been investigated for both endothermic and exothermic reactions [39].

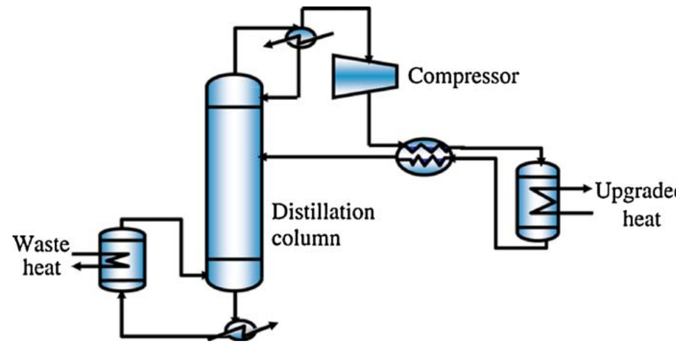


Fig. 6. Isopropanol–acetone–hydrogen chemical heat pump (IAH-CHP) [63].

Most of studies concentrate on the type of material that used as a catalyst for both the reactions and the working pairs reaction system, in a usual case, one reaction is easy to proceed; however, the other reaction is difficult to proceed because of the restriction of a chemical equilibrium for reversible reaction. Fig. 6 shows isopropanol/acetone/hydrogen chemical heat pump system (IAH-CHP) [63]. The endothermic reaction is dehydrogenation of isopropanol, taking place at 80–90 °C, and the exothermic reaction is hydrogenation of acetone, taking place at 150–210 °C. The reaction equations are shown as follows:

$$(CH_3)_2CHOH^{s}_{(l)} \rightarrow (CH_3)_2CO_{(g)} + H^{s}_{2_g} \quad \Delta H = 100.4\,\text{kJ/mol} \qquad (1)$$

$$(CH_3)_2CO_{(g)} + H^{s}_{2_g} \rightarrow (CH_3)_2CHOH^{s}_{(g)} \quad \Delta H = -55.0\,\text{kJ/mol} \qquad (2)$$

The development of a demonstration unit of an isopropanol–acetone–hydrogen chemical heat pump system has been studied by Itikorn and Pornpote [63], the study was divided into four parts, the dehydrogenation, the hydrogenation, the distillation unit and the system when all the components were connected together. For the first two parts the studies of isopropanol dehydrogenation and acetone hydrogenation, the equipment setup was arranged as shown in Fig. 7. For dehydrogenation, isopropanol was fed to a tubular reactor by pumping through a peristaltic pump. It was then passed into an oil bath that was kept at a certain temperature, 80 °C, before entering the reactor. For hydrogenation of acetone, the equipmental setup was similar to the dehydrogenation setup in Fig. 6. Isopropanol was pumped through a peristaltic pump, while acetone was pumped through a PTFE diaphragm pump. They were mixed before passing through the oil bath that was kept at a certain temperature and entered the exothermic reactor. The results showed that the conversions in the endothermic and exothermic reactors were 8.5% and 11.6%. The temperature was raised from 80 °C to 136 °C.

Kato et al. [64] has been developed a magnesium oxide/water chemical heat pump, where the endothermic reaction temperature takes place at 373–423 K and the reaction vapor pressure 12.3–47.4 kPa. The reaction system of the heat pump required is:

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s), \quad \Delta H = -81.02\,\text{kJ/mol}. \qquad (3)$$

The principle underlying this heat pump is shown in Fig. 8. The pump consists of a magnesium oxide reactor and water reservoir, and has two operation modes: heat storage and heat output [65].

A magnesium oxide/water chemical heat pump was expected to be applicable to load leveling in a common cogeneration system by storing chemically surplus heat during low heat demand and supplying heat during peak load periods [65,66]. A chemical heat pump using a magnesium oxide/water reaction system was expected to be applicable to cogeneration systems using gas engine, diesel engine, and fuel cells.

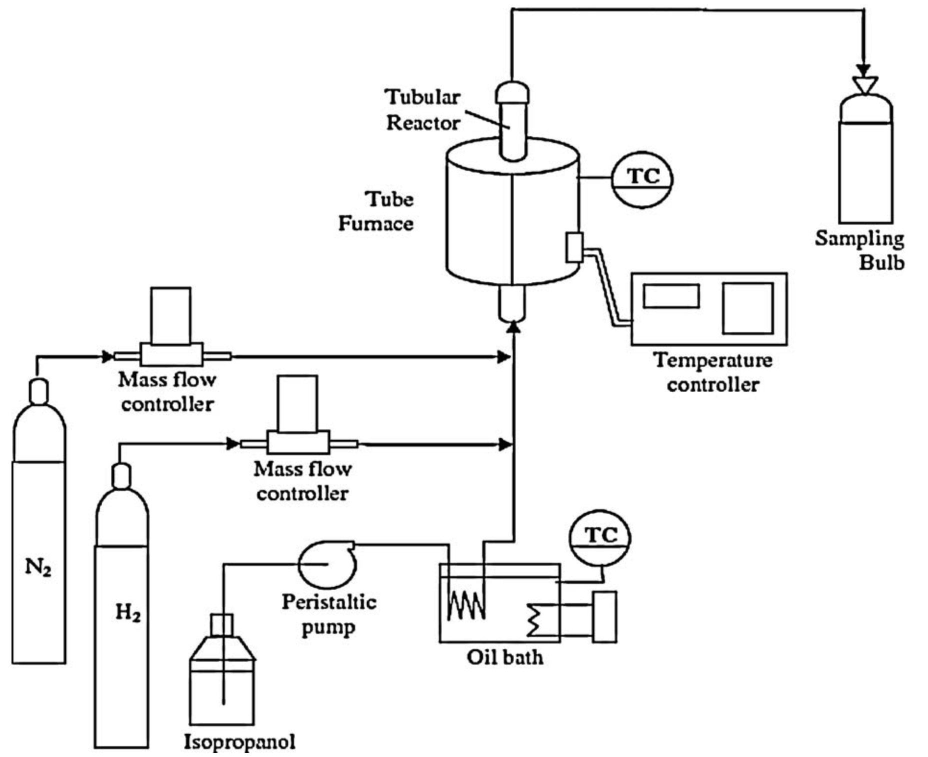


Fig. 7. Experimental setup for dehydrogenation of isopropanol and hydrogenation of acetone [63].

The CHP system with paraldehyde/acetaldehyde (Pa/A) has presented for cooling system Fig. 9. This system consists of four parts; an endothermic reactor, an exothermic reactor, a compressor and an expansion valve. The depolymerization is endothermic and reversible as Eq. (4).

$$\text{Paraldehyde(2, 4, 6-trimethyl-trioxane)(l)} \leftrightarrow \text{3acetaldehyde(l)} \quad \Delta H^0_{298} = 110.3\,\text{kJ}\,(\text{mol-pa})^{-1} \tag{4}$$

The vaporization of acetaldehyde is also endothermic as Eq. (5).

$$\text{Acetaldehyde(l)} \leftrightarrow \text{acetaldehyde(g)} \quad \Delta H^0_{298} = 26.4\,\text{kJ}\,(\text{mol-A})^{-1} \tag{5}$$

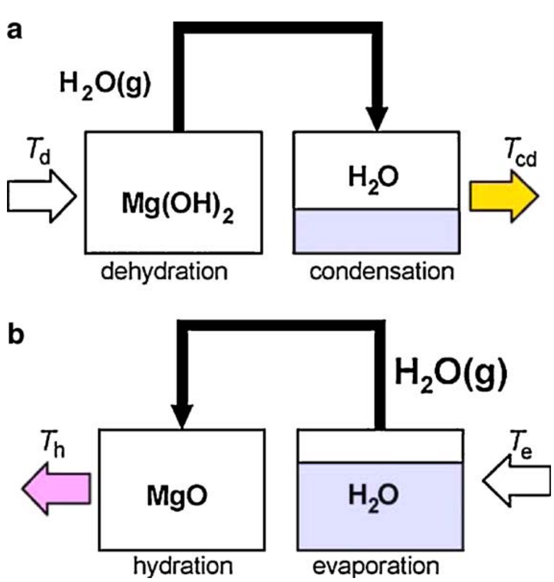


Fig. 8. Principle underlying the chemical heat pump: (a) heat storage mode, (b) heat output mode [65].

Paraldehyde is depolymerized with an acid catalyst, and acetaldehyde vapor is generated in the endothermic reactor and the acetaldehyde vapor is compressed and fed to the exothermic reactor. In the exothermic reactor, acetaldehyde is trimerized on the acid catalyst and then forms liquid paraldehyde. The generated heat in the exothermic reactor is released to the atmosphere. The liquid paraldehyde is returned to the endothermic reactor through the expansion valve to complete the cycle [16].

For high-temperatures, a calcium oxide/lead oxide and PbO/CO_2 reaction system has been investigated [67]. The system consists of CaO and a PbO reactor has two modes; heat storage mode and heat supply mode as shown in Fig. 10. In the storage mode, the CaO reactor receives heat (Q_{d1}) from a heat source at temperature T_{d1}.

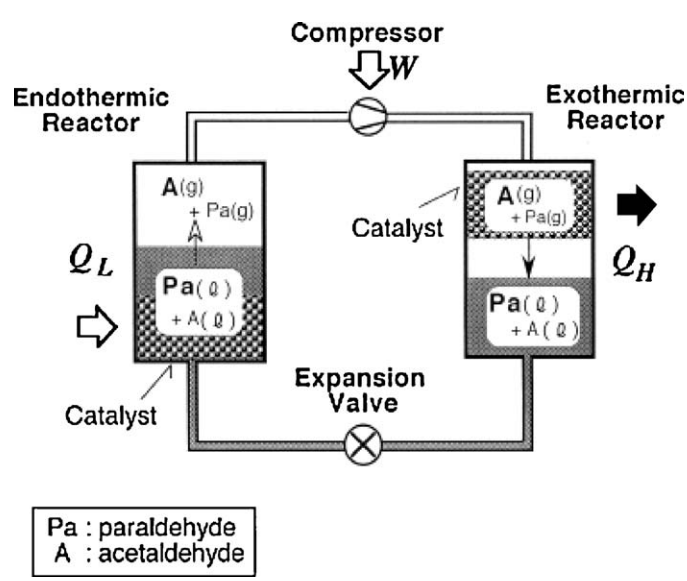


Fig. 9. Schematic diagram of the Pa/A systems [16].

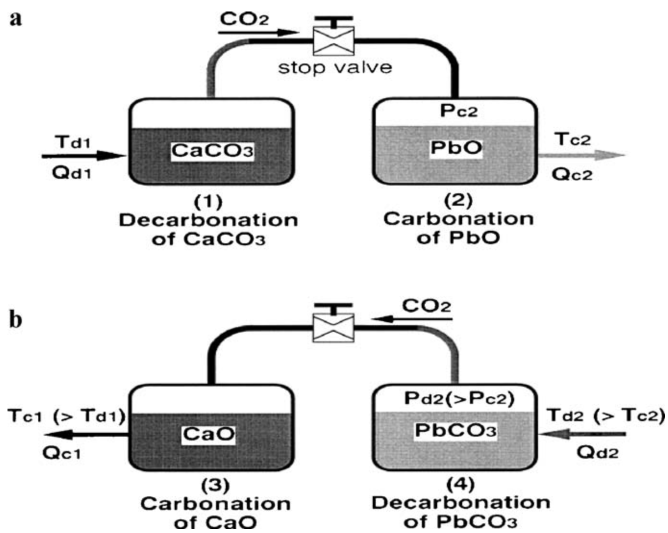


Fig. 10. Principle of CaO/PbO/CO_2 chemical heat pump (a) heat storage mode (b) heat output mode [67].

Subsequently, CaO and CO_2 are formed as a result of the decarbonation of $CaCO_3$. The CO_2 is reacted with PbO in the PbO reactor at some pressure (P_{c2}) and the exothermic heat of the carbonation is recovered at temperature T_{c2}, yielding $PbCO_3$. In the heat supply mode, the decarbonation of $PbCO_3$ proceeds in the PbO reactor using heat at temperature T_{d2}, which is higher than T_{c2}. The CO_2 formed at pressure P_{d2}, which is higher than P_{c2}, is introduced into the CaO reactor. Carbonation of CaO then proceeds and heat (Q_{c1}) is generated exothermically in the reactor at a temperature of T_{c1}, which is higher than T_{d1}, due to the higher reaction pressure. The reaction for this pair is:

$$CaO(s) + CO_2(g) = CaCO_3, \quad \Delta H^0_{298} = -178.321\,\text{kJ/mol} \tag{6}$$

$$PbO(s) + CO_2 = PbCO_3, \quad \Delta H^0_{298} = -88.27\,\text{kJ/mol} \tag{7}$$

In the case of continues type liquid–gas CHP, the exothermic reaction heat is produced at high temperature, whereas the endothermic reaction heat and the evaporation heat are supplied at low temperature for the decomposition of metal hydride [39,43].

3.2. Solid–gas CHP

In the solid–gas chemical heat pump, the general reaction taking place in the reactor is of the form [68]:

$$S + nG \leftrightarrow S' + n\Delta H_r \tag{8}$$

where the synthesis and decomposition reactions occur at two different temperatures corresponding to different pressures. It is noted that solid–gas reaction equilibrium and the liquid–vapor equilibrium are both mono-variant systems, which can be described the Clausius–Clapeyron equation:

$$\ln(P) = \frac{-\Delta H_r}{RT} + \frac{\Delta S}{R} \tag{9}$$

In Clapeyron diagram, they are expressed as two straight lines. The thermodynamic cycles of heat transformers can be fixed in Clapeyron diagram if the certain working pairs and working conditions (e.g. pressure or temperature) are known [68]. The CHP operates between three different temperature levels: low temperature *Te*, middle temperature *Tc*, and high temperature *Tg*, two different pressures: low pressure *Pe* and high pressure *Pc*, as illustrated in the Clausius–Clapeyron diagram in Fig. 11.

Various chemical substances can be used in the solid–gas heat transformers [68], and Table 1 gives some main working

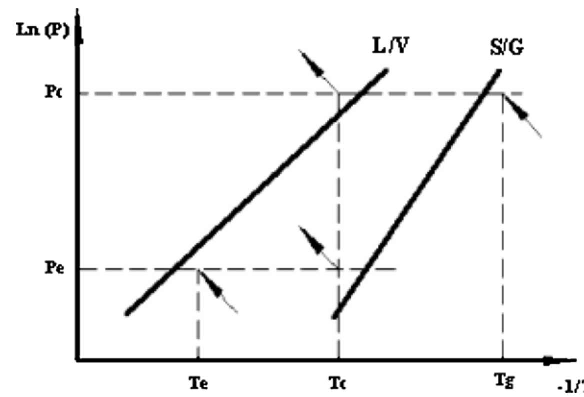


Fig. 11. Diagram of Clausius–Clapeyron.

pairs according to different reactive gas. There are ammonia system (alkaline salts/ammonia, alkaline earth salts or metallic halides/ammonia, nitrates or phosphates/ammonia, monomethylamine/ammonia), sulfur dioxide system (oxides/sulfur dioxide), water vapor system (oxide/water vapor, salts/water vapor), carbon dioxide system (oxides/carbon dioxide), hydrogen system (metals or metal alloys/hydrogen), etc. The mostly used working pairs are metal hydride/hydrogen and chloride/ammonia, whose ozone depletion potential (ODP) and global warming potential (GWP) are all zero [69].

Solid–gas heat transformers can be widely used in many fields. American BNL (Blackburn National Laboratory) has ever found that calcium chloride/methanol, magnesium chloride/water vapor, ammoniate/ammonia and metal hydride/hydrogen systems could be used in effective utilization of industrial waste heat and solar energy decades ago [70]; and it was reported that according to "Super heat pump, energy cumulation plan (1984)", Japan recovered waste heat which accounted for 50% of consumed energy [70]. Moreover, the high-grade heat from heat transformers can drive absorption and adsorption refrigeration or heat pump systems, so as to get better performance than those driven by the waste heat or solar energy directly; besides, when the temperature of high grade heat is higher than 120 °C, it can be used to produce steam, and when higher than 230 °C, the steam can even drive the MP-steam grid to generate electricity [71]. Solid–gas heat transformer system can also store middle-grade heat easily in working pairs by decomposition reaction and release energy again when necessary by synthesis reaction to balance the time and space conflicts between heat supply and demand to improve energy use [72].

3.2.1. Metal hydrides system

Metal hydride forming alloys and the respective hydrides can be used as working material in very different technical applications, i.e. as electrodes in batteries\ as hydrogen storage materials, in gas purification devices and in thermally driven hydrogen compressors and thermodynamic machines. Elemental metals and/or many metal alloys react with hydrogen and form a metal hydride phase (metal-to-hydrogen bonding). Exothermic reaction takes place when hydrogen is absorbed by a hydride and heat is liberated, while cooling is provided due to desorption of hydrogen gas from hydride. Metal hydride absorbs large amounts of hydrogen gas and could also be used for hydrogen storage [39]. There are already many applications of the single-stage metal hydride/hydrogen heat transformer as shown in Table 2 [73]. MPD Technology Corp in America developed a heat transformer of $LaNi_5/LaNi_{4.7}Al_{0.3}$ type alloys which is drived by middle-grade heat at 60 °C, cooled by cold source at 20 °C, and can export water or steam of 3.5 kW at 90–100 °C; two Japanese companies worked out the continuous$LaNi_{4.7}Al_{0.3}/LaNi_5$

Table 1
Classification of solid–gas thermo-chemical systems [68].

Ammonia system	Sulfur dioxide system	Water vapor system	Carbon dioxide system	Hydrogen system
Alkaline salts (e.g. NaOH)/NH_3 Alkaline earth salts (e.g. $CaCl_2$); metallic halides (e.g. $MnCl_2$, $NiCl_2$)/NH_3 Nitrates, phosphates/NH_3 Monomethylamine/NH_3	Oxides (e.g. CaO)/SO_2	Oxides (e.g. MgO, CaO, Na_2O)/H_2O Salts (e.g. $CaCl_2$, Na_2S)/H_2O	Oxides (e.g. CaO, BaO, PbO)/CO_2	Metals (e.g. Ca, Ni, Mn, Al)/H_2 Metal alloys (e.g. $LaNi_5$)/H_2

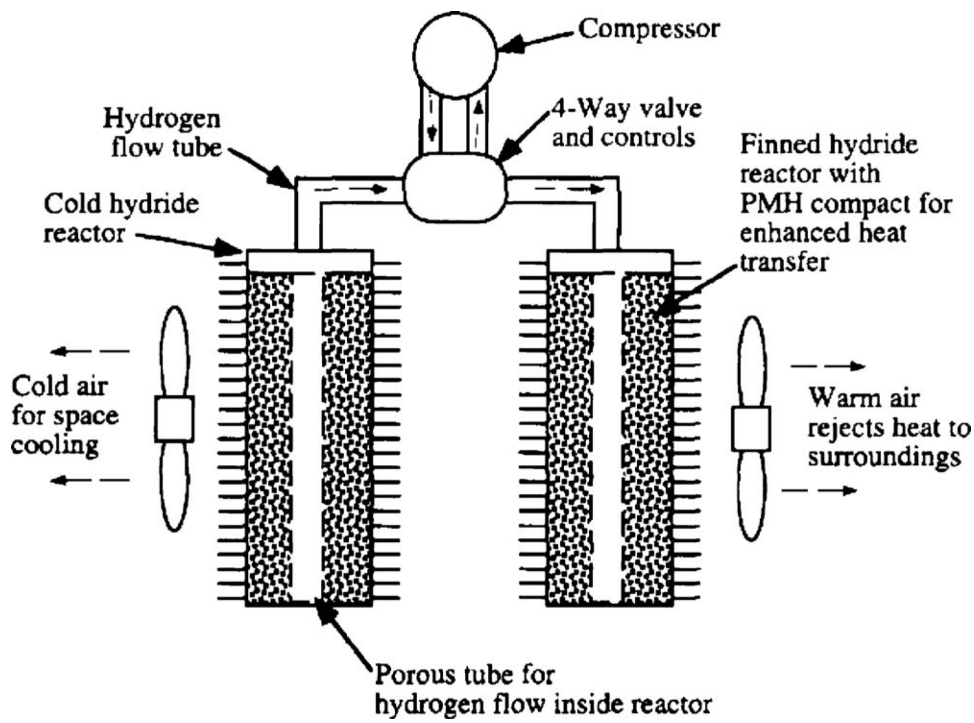


Fig. 12. Schematic drawing of hydride heat pump [74].

heat transformer system whose cycling time is 6 min, COP was 0.38 and temperature lift was 15–25 °C [68].

Kim et al. [74] have developed a compressor-driven hydrogen metal-hydride heat pump system utilizing hydride reactors (Fig. 12). This achieves higher efficiency and appears to have competitive life-cycle costs as compared to conventional refrigeration system. Testing this system with 500 full cycle operations shows that the performance does not degrade and the specific cooling power obtained could reach 1.5 kW/kg of $LaNi_5$.

Enhanced internal heat transfer in the hydride reactor both within the hydride bed and between the hydride bed and the external heat exchanger is required. To improve the heat transfer in reactor, the hydride-forming metal particles are coated with a thin layer of copper (around 1 μm thickness) and then compressed and sintered into a porous powder of metal hydride (PMH) compact. The hydride reactors containing PMH compact are sintered into lightweight finned tubes, and air is forced over the exterior to transfer heat to surroundings [39].

Kang and Yabe [75] reported a continuous metal-hydride heat transformer, which contains two pairs of reactors of metal hydrides ($LaNi_5$ at lower temperature and $LaNi_{4.5}Al_{0.5}$ at higher temperature). The reactors are made of bundles of tubes and are fabricated as cylindrical tubes. Heat transfer medium flows through the inner tube to supply and extract heat to and from the reactors. The reactors are packed by hydride material, of inner diameter R_1 and outer diameter R_2. This hydride material is surrounded by a fine net to allow hydrogen to pass through. The performance of this heat transformer system is predicted based on heat and mass balances and

Table 2
Products of metal hydride/hydrogen heat transformer [73].

Alloys	Working performance					Developer
	Temperature (°C)			Cycling time (min)	COP/power (kW)	
	T_b	T_m	T_l			
$LaNi_5/LaNi_{4.7}Al_{0.3}$	90–100	60	20		3.5	Put into use; developed by American MPD Corp
$MmNi_{4.15}Fe_{0.85}/LaNi_5$	140–180	50–95	20–36		3.5	Developed by American Solar Turbines International
$LaNi_{4.9}Al_{0.1}/TiFe_{0.8}Ni_{0.2}$	58	42	15	3–6	50	Phototype; developed by Sweden Studvik Engergiteknik AB
$LaNi_{4.7}Al_{0.3}/LaNi_5$	90	65–75	15–25	6	0.38/3.5	Liquid–liquid heat exchanger; developed by two Japanese companies

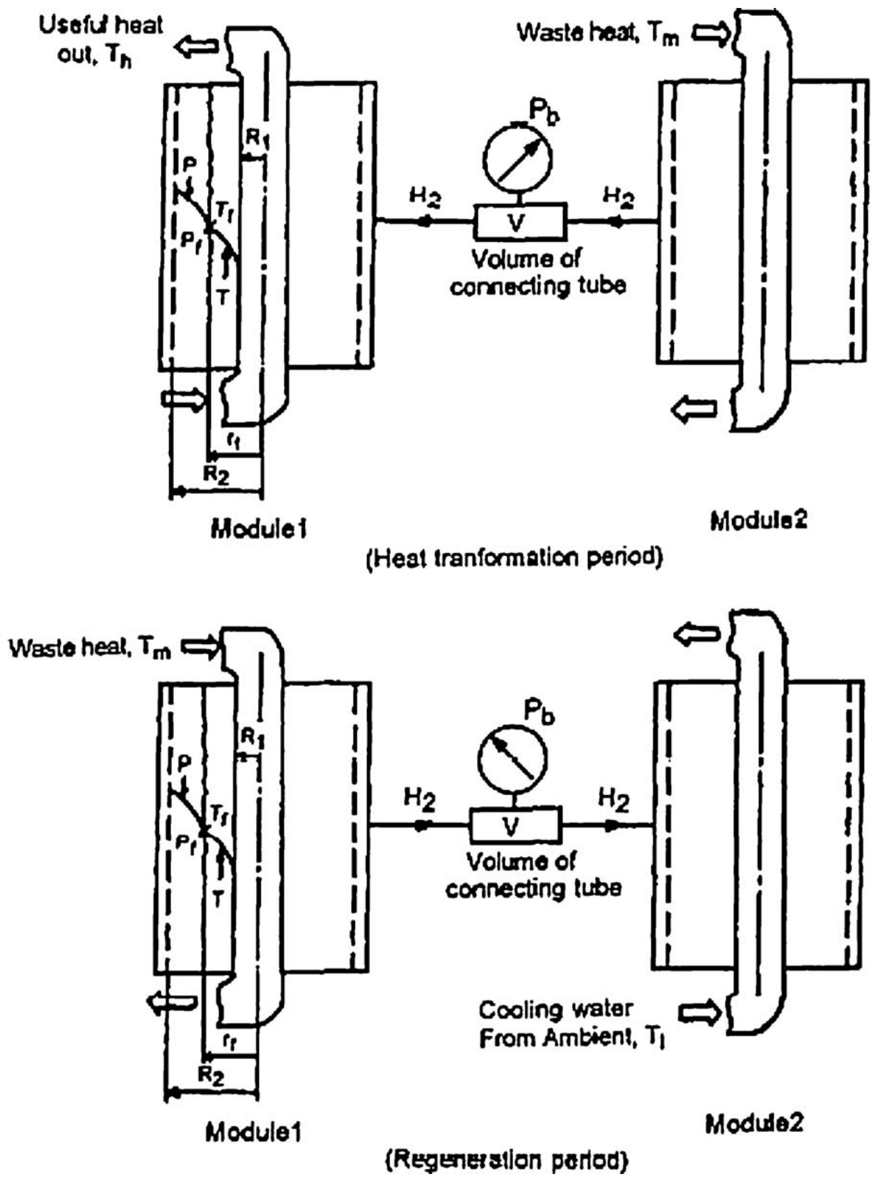


Fig. 13. Physical model for a module-type of metal-hydride heat transformer [75].

thermodynamic properties of hydride material and hydrogen. The physical model and geometric configuration are shown in Fig. 13. A pair of reactor modules works for upgrading heat and, in turn, endures a regeneration process. Practical reactors are made of a bundle of tubes. However, the reactor module is considered as cylindrical double-tubes; the heat transfer medium flows through the inner tube to supply or to extract heat to/from a reactor module. Hydride materials are stacked compactly between tubes and surrounded by a fine mesh of screen net to give a room for hydrogen passage between a net and the outer tube. An insulation tube is fitted to the inner wall of the outer tube to segregate the thermal inertia of the outer tube.

3.2.2. Metallic salt-ammonia system

Metallic salt-ammonia systems have been widely used as solid–gas reaction pairs for CHPs. Ammonia is the usual adsorbate of metal chlorides. During the adsorption process, salt swelling and agglomeration can occur and influence the heat and mass transfer performance. The advantages of metal chlorides/ammonia are simple and compact configuration, less requirement for temperature level of the driven heat reservoir, short cycling time, etc. [76], and the large adsorption quantity, which is higher than 1 kg/kg for most chlorides [77]. So it is suitable for the use of solar energy or industrial waste heat. The disadvantage of metal chlorides/ammonia as working pair is mainly related to the salt swelling and agglomeration during adsorption, which compromises the heat and mass transfer [77], and lie in problems caused by irritating smell, corrosion and high system pressure [76].

For ammonia-based system utilizing chloride salts (alkaline, alkaline-earth or metallic), the heat of reaction are of the same order of magnitude, typically $\Delta H_r = 50 \pm 15$ kJ/mol. However, the enthalpy of evaporation or condensation of the ammonia gas is only about half of this. The reaction in chloride salts bed of ammoniated system takes place within the operating pressure range up to 50 bar, temperature range of (−50 °C to 300 °C), and depends on the number of moles of gas reacting per mole of salt compound [78].

In recent publications a number of mathematical models for solid–gas CHPs have been described [79]. The first model was developed by Lebrun and Spinner [52] to simulate the basic cycle. It has been used to design a 20–50 kW unit. Valkov [80] used the same approach to simulate the results of a 5 kW chemical heat pump.

For simulation of the dynamic behavior of the gas–solid fixed-bed reactors used in chemical heat pumps (CHPs), Hua et al. [81] have been presented a model coupled the chemical kinetics with heat transfer. The model can be used to simulate the dynamic local temperatures and advancements of the reactive medium, and the global advancements, etc. It can also be used to determine the influence of various parameters on the reactor performances, including the kinetic and thermal parameters, the operational parameters, and the configuration parameters of the medium or the reactor. The system mainly consists of a cylindrical reactor and an evaporator/condenser. $SrCl_2$–NH_3 is working pair of this model.

A numerical model has been developed to simulate the fixed bed solid–gas reactor ($MnCl_2$–NH_3) in a CHP. It was based on the rate of the overall process being controlled by the rate of heat transfer. The model used a general finite volume procedure which is easy to modify if changes are required. The model has been used to calculate performance characteristics of CHP reactors, such as conversion of the salt and power produced. The results has shown that the reactor radius has an important effect on the volumetric power of the reactor, the duration of the reaction cycle, the amount of heat exchange area required, and heat losses [79].

The unsteady state overall heat transfer coefficient in a chemical heat pump reactor (NH_3–$CoCl_2$) has been studied by Aidoun and Ternan [82], in this study, the thermal inertia could be determined experimentally, as the difference between the instantaneous rate of heat generated by reaction (the change in weight of the reactor measured by a load cell multiplied by the molar heat of reaction) and the heat transferred (measured by the cooling water flowrate and its change in temperature).

Bougard et al. [83] introduced a single-stage two-salt prototype with working pairs of $CaCl_2$ (8-4)/$ZnCl_2$ (4-2) NH_3, which upgraded middle-grade heat from 80–100 to 150–200 °C. It was reported that the measured system pressure was well fitted with the theoretical one.

For different working pairs used in ammonia-based reacting system of CHPs, Table 3 [41] shows the Upgraded temperature in heat transformer system of various working pairs of two connected reactors system, the operating conditions are, in the pressure range between 0.1 and 50 bar and temperature lifts of at least 40 °C. When the heat source temperature is lower than 100 °C the possible reactive salts are $CaCl_2$–$MnCl_2$, $BaCl_2$–$CaCl_2$ and $CaCl_2$–$NiCl_2$. Reactor(s) containing chloride salts of Mn and Ni give the highest output temperature (maximum of 235 °C), but the temperature source must be greater than 100 °C [39].

Table 3
Upgraded temperatures of different working pairs used in ammonia-based reacting system of CHPs [41].

Couple of chloride salts[a]	Upgraded temperature (low temperature (T_l) to high temperature (T_h)) [°C]
$CaCl_2$(4/2) and $MnCl_2$(6/2)	90–125
$BaCl_2$(8/0) and $CaCl_2$(4/2)	90–120
$CaCl_2$(8/4) and $MnCl_2$(6/2)	100–135
$CaCl_2$(8/4) and $FeCl_2$(6/2)	120–185
$MnCl_2$(6/2) and $NiCl_2$(6/2)	130–195
$CaCl_2$(4/2) and $MgCl_2$(6/4)	145–215
$MnCl_2$(6/2) and $NiCl_2$(6/2)	155–220
$MnCl_2$(6/2) and $NiCl_2$(6/2)	155–235

[a] The low temperature heat sink is 15 °C except for the last couple, which is 35 °C.

The simplest way to achieve temperature lift in the solid–gas CHP is the basic thermodynamic cycle [84], which consists of a reactor, where the solid–gas synthesis or decomposition reaction happens, and a heat exchanger, where the evaporation or condensation of the gas takes place, as shown in Fig. 14. The cycle is described by a liquid/vapor equilibrium line (L = V line) and a solid/gas reaction equilibrium line (S = G line) in Clapeyron's diagram in Fig. 14a.

4. Overview of CHP dryer

The CHPD has been discussed from the view point of coupling the CHP and direct dryer, the efficiencies of various types of CHPD systems were evaluated on the bases of energy consumption [15,85,86]. Rolf and Corp [87] developed a CHPD for drying of bulky material such as bark and lumber. This method of drying is easy to adapt to any industrial drying process, but in particular the drying processes in the pulp and paper industry.

The CHP has four possible operating modes according to the operating pressure levels: heat-storage mode, heat-enhancement mode, refrigeration mode, and temperature-upgrade mode. The

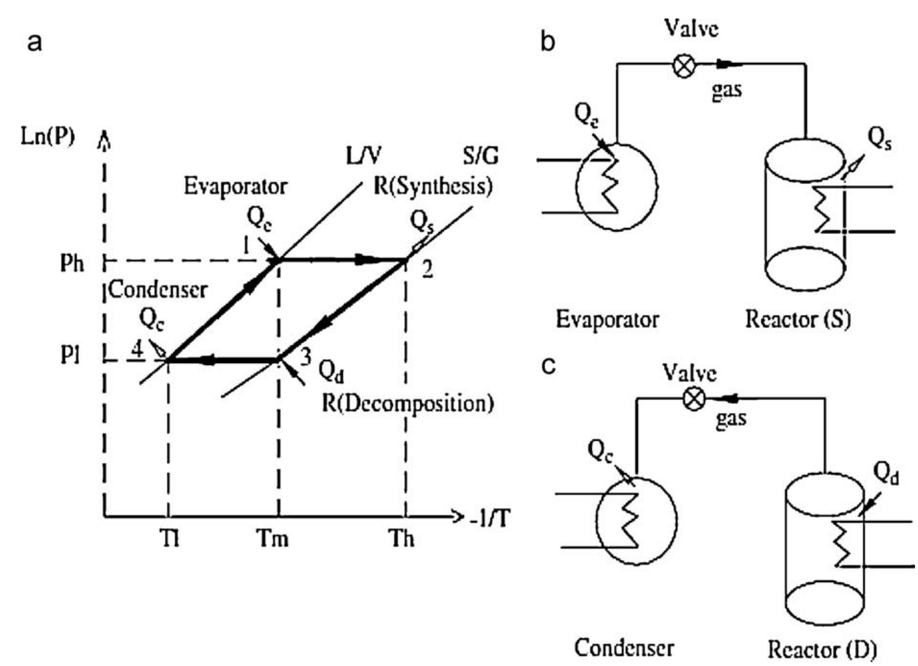


Fig. 14. Clapeyron's diagram showing operation mode of basic single-stage heat transformer [84].

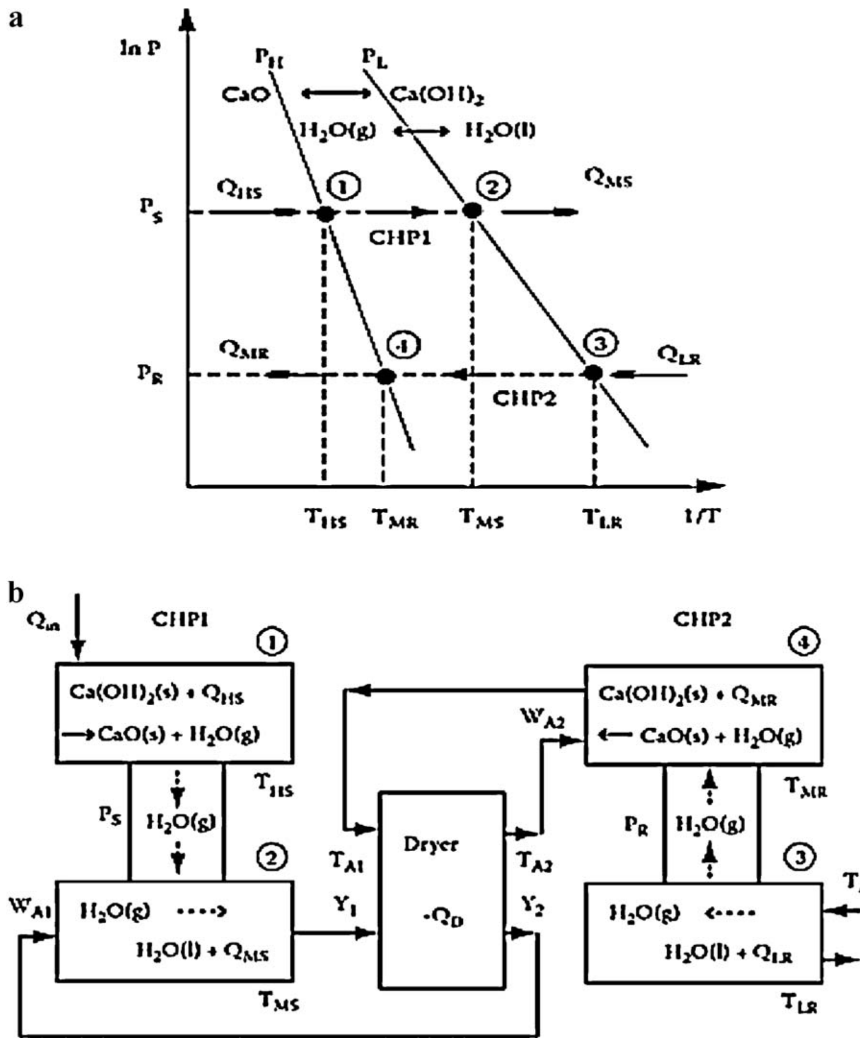


Fig. 15. CHPD system using $CaO/H_2O/Ca(OH)_2$ reaction operating in heat enhancement mode (a) operating line (b) flowsheet [85].

actual operating pressures and temperatures of CHPs depend on the reaction equilibrium values-they are governed by the thermodynamics of the system chosen [88].

Ogura and Mujumdar [15] illustrated the CHPD idea by selecting the calcium oxide/calcium hydroxide reaction from the viewpoints of their safety, reactivity, reaction enthalpy, and reaction equilibrium temperature–pressure level, and material cost. The reaction was used in this study is:

$$CaO(s) + H_2O(g) \Leftrightarrow Ca(OH)_2(s) + 104.2\,kJ/mol \quad (10)$$

$$H_2O(g) \Leftrightarrow H_2O(l) + 41.7\,kJ/mol \quad (11)$$

The CHPD system which was proposed is shown in Fig. 15 [85]. Fig. 15a shows the operating line for this CHPD indicating the relationships between the reaction equilibrium pressure and temperature. P_P is the reaction equilibrium pressure at the reaction temperature of CaO. P_W denotes the saturated vapor pressure calculated from the water temperature on the evaporator/condenser. This system works in the heat enhancement mode. CHP1 and CHP2 operate concurrently. In this Fig. 15a, CHP1 is in the heat-storing step and CHP2 is in the heat-releasing step. These CHPs switch the steps with each other every hour or so; the switching time is decided by CHP experiments. Fig. 15b shows a flowsheet of the corresponding CHPD. In CHP1, high temperature heat $Q_{H,S}$ is stored in the CaO reactor using any type of heat source with Q_{in} at $T_{H,S} > 594\,^{\circ}C$. Water vapor in the reactor is released from the reactor and is condensed in the condenser. The condenser releases medium temperature heat $Q_{M,S}$ around $T_{M,S} = 150\,^{\circ}C$ by controlling the heat transfer rate. On the other hand, CHP2 also releases medium temperature heat $Q_{M,R}$ around $T_{M,R} = 360\,^{\circ}C$ in the CaO reactor by controlling the evaporator temperature at around $T_{L,R} = 20\,^{\circ}C$ with room temperature heat. In short, this CHP system stores the 600 °C heat and releases 150 °C and 360 °C heats continuously by switching the CHP steps.

When the CHPs work in the heat-enhancement mode, the released energy from the CHP2 can be >200% of the stored heat in CHP1, depending on the chemical system selected [88]. On the contrary, when the temperature of the released heat from CHP2 is required to be much higher than that of the stored heat in CHP1, the temperature-upgrade mode is especially effective. In addition to the choice of CHP modes, one must select the candidate reactions considering the reaction temperature, the pressure level, reactivity, reaction reversibility, safety, corrosion, costs, etc. This means that the features of the reaction system determinate the features of the CHPD system. Ogura et al. [89] presented the results of an experimental investigation on the controllability of hot air produc-

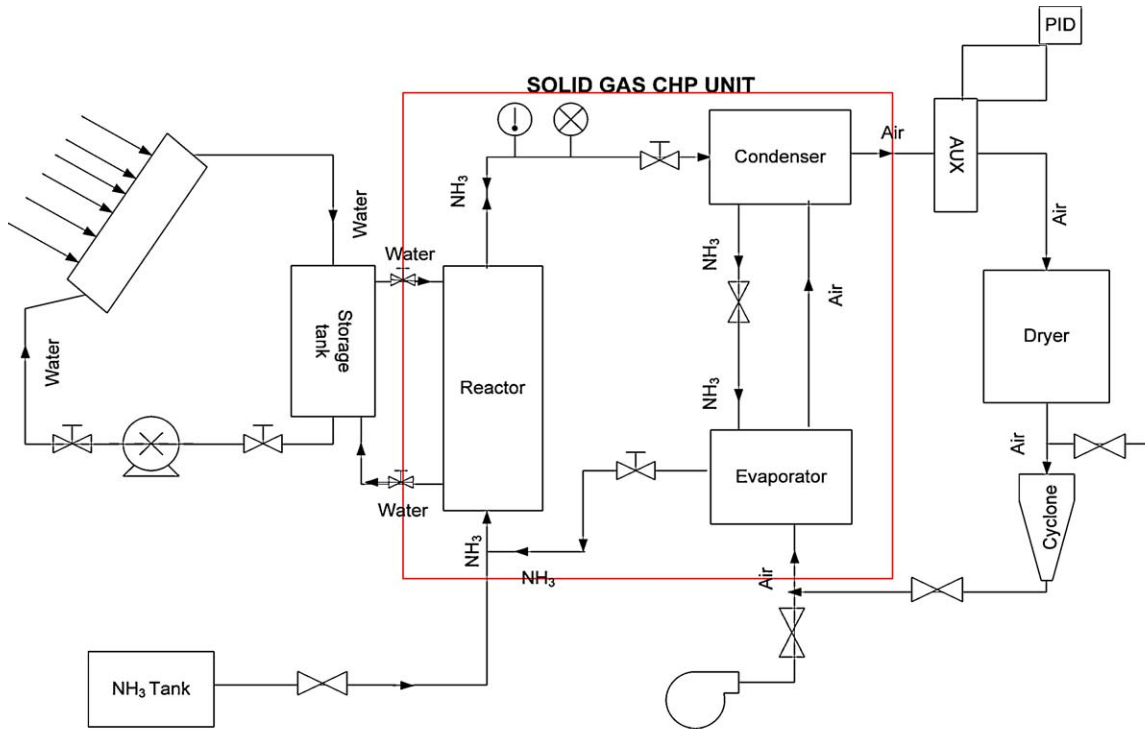


Fig. 16. Schematic diagram of solar assisted chemical heat pump dryer [90,91].

tion, and proposed that the heat air temperature can be controlled by adjusting the reactor temperature, and pressure, as well as thermal power supplied to it. It is shown that hot air can be produced in both heat storage and heat release steps of the CHP.

5. Advanced of solar assisted chemical heat pump dryer (SACHPD)

Solar drying system with solid–gas chemical heat pump (SACHPD) has been proposed by Ibrahim et al. [90,91]. Fig. 16 shows the schematics of a solar-assisted solid–gas chemical heat pump dryer. The system consists of four mean components solar collector (evacuated tubes type), storage tank, chemical heat pump unit and dryer chamber. The reaction used in this study is:

$$CaCl_2 \cdot 2NH_3 + 6NH_3 \rightarrow CaCl_2 \cdot 8NH_3 + 6\Delta H_r \quad (12)$$

The drying chamber contains multiple trays to hold the drying material and expose it to the air flow. The general working of chemical heat pump in this study occurs in two stages: adsorption and desorption. The adsorption stage is the cold production stage, and this is followed by the regeneration stage, where decomposition takes place. During the production phase, the liquid–gas transformation of ammonia produces cold at low temperature in the evaporator. At the same time, chemical reaction between the gaseous ammonia and solid would release heat of reaction at higher temperature. The incoming air is heated by condensing refrigerant (ammonia) and enters the dryer inlet at the drying condition and performs drying. After the drying process, part of the moist air stream leaving the drying chamber is diverted through the evaporator, where it is cooled, and dehumidification takes place as heat is given up to the refrigerant (ammonia). The air is then passing through the condenser where it is reheated by the condensing refrigerant and then to the drying chamber.

Ibrahim et al. [90,91] has been developed the mathematical models for different components of the solar assisted chemical heat pump dryer. In the solar collector the useful energy gain of collector surface area is given by the following equation:

$$Q_u = \eta A_C I \quad (13)$$

The collector efficiency for the evacuated tube collector is given by:

$$\eta_{eva} = 0.84 - 2.02(T_m - T_a)/I - 0.0046[(T_m - T_a)/I]^2 \quad (14)$$

The heat loss from the tank on ground is calculated by:

$$Q_s = (UA)_{strg}(T_l - T_a) \quad (15)$$

In the chemical heat pump heat is supplied to the reactor at high temperature to regenerate ammonia which will then be condensed in the condenser at medium temperature, the heat required to evaporator at low temperature is supplied to vaporize ammonia, which reacts with salt and release heat at medium temperature. The heating performance for chemical heat pump could be defined as:

$$COA = \frac{Q_c + Q_r}{Q_r} = \frac{\Delta H_c + \Delta H_r}{\Delta H_r} \quad (16)$$

where Q_c is the condenser heat rejection, Q_r is the reaction heat and ΔH_c is the enthalpy of condensation. Therefore, for the integrated chemical heat pump with solar collector and storage tank the heating performance of chemical heat pump could be:

$$COP^h = \frac{Q_c + Q_r}{(Q_u - Q_s) + Q_r} \quad (17)$$

The solar fraction (SF) is defined as the utilized solar heat divided by the total heat demand and calculated from the following relationship:

$$SF = \frac{[Q_u - Q_s]}{Q_c} \quad (18)$$

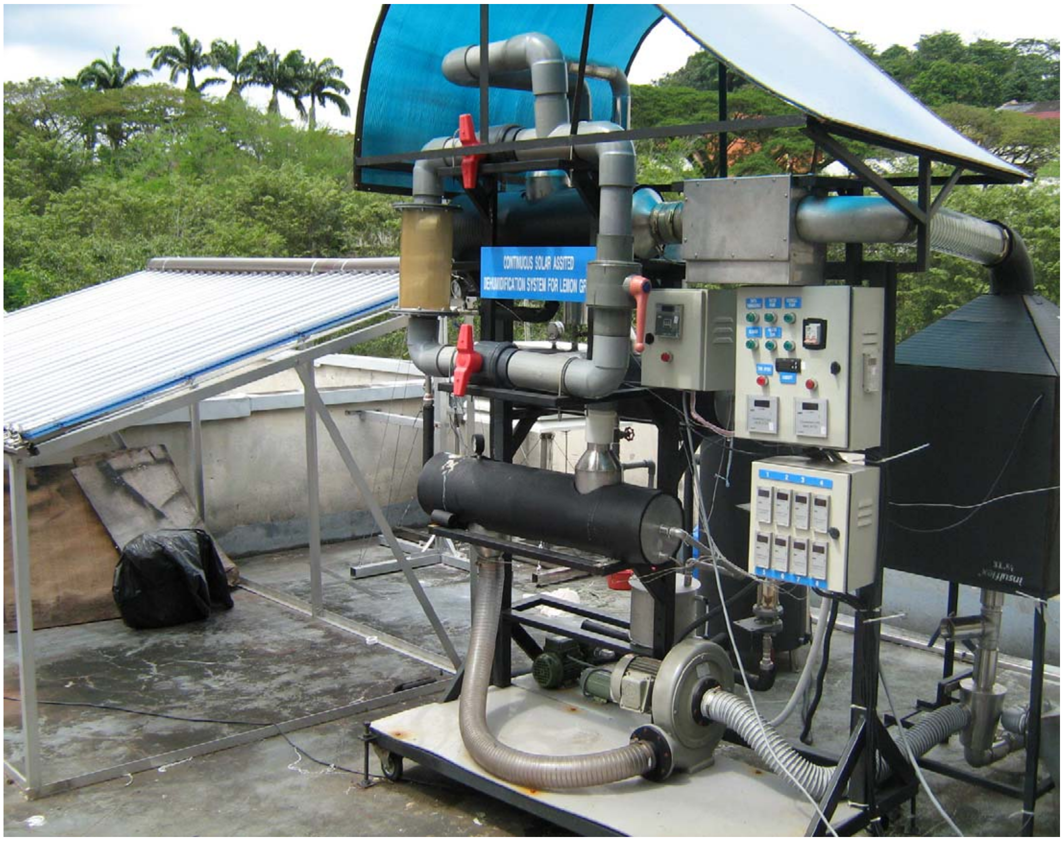


Fig. 17. Photograph of the experimental set-up [92,93].

The experimental results of the performance of the system under various Malaysian climatic conditions have been presented [92,93]. The system is located on the roof top of a three-storey building at the National University of Malaysia (Universiti Kebangsaan Malaysia). Fig. 17 shows the photograph of the experimental set-up.

A series of experiments has been performed on the system to evaluate the performance. The performance of the system has been investigated experimentally for different environment climate conditions. Two representative days for clear and cloudy conditions were presented [92]. Fig. 18 shows the hourly average values of solar radiation for typical clear and cloudy days in December for Malaysia, while Fig. 19 shows the average values of ambient temperature for the same days. Fig. 20 shows the experimental comparison of solar fraction for clear and cloudy days. As seen from the figure that the maximum value of solar fraction for clear day is 0.713 against maximum value of 0.322 for cloudy day. Fig. 21 shows the experimental performance of coefficient of Performance of chemical heat pump (COP^h) for clear and cloudy days. As seen in the figure a maximum value of (COP^h) of 2 for clear day is found against maximum (COP^h) of 1.42 for cloudy day. Fig. 22 shows the system energy output over about 9 h drying time, which found the total energy output is 51 kWh for clear day against 25 kWh for cloudy day [92]. The results show that any reduction of energy at condenser as a result of the decrease in solar radiation will decrease the coefficient of performance of chemical heat pump as well as decrease the efficiency of drying.

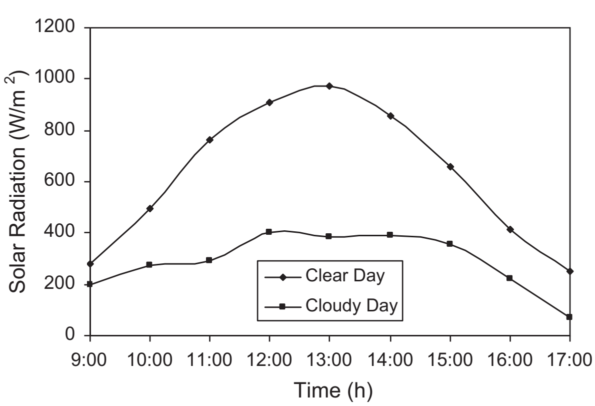


Fig. 18. Average hourly radiation in Malaysia in December.

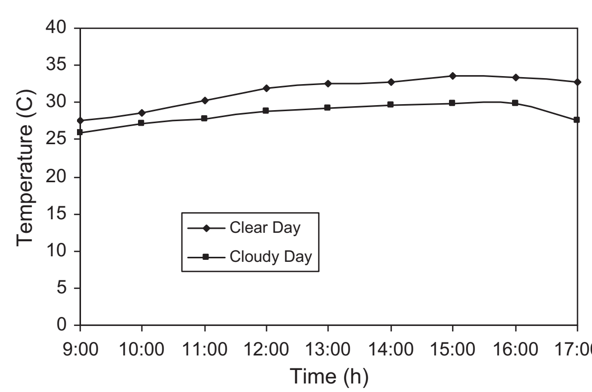


Fig. 19. Average ambient temperature in Malaysia in December.

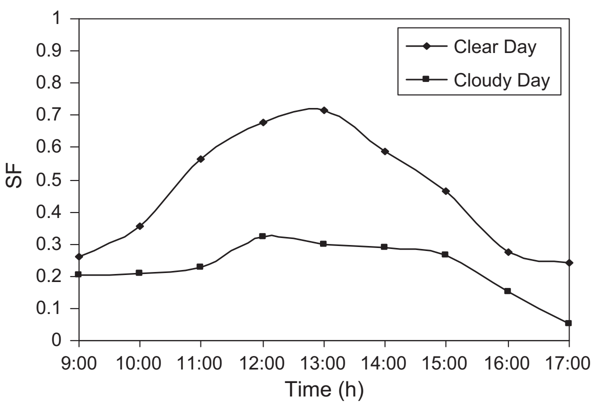


Fig. 20. System solar fraction.

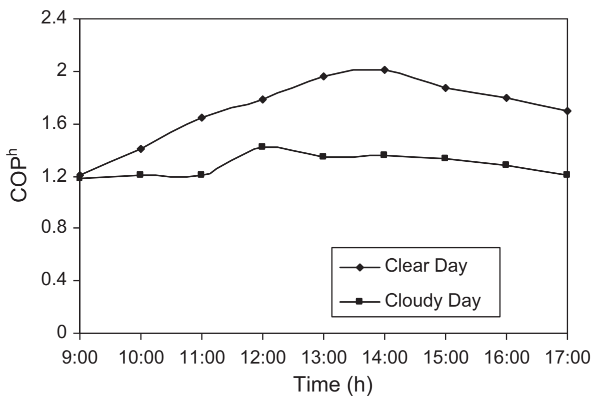


Fig. 21. Coefficient of performance of chemical heat pump.

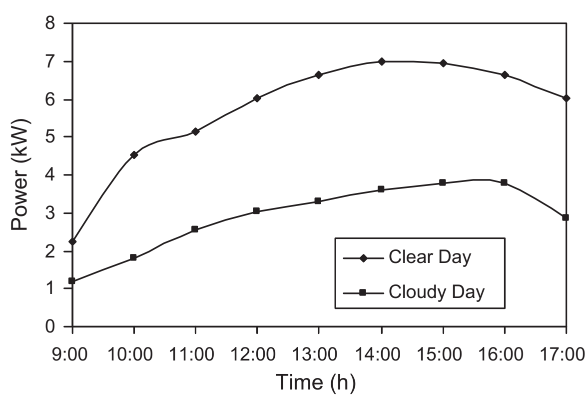


Fig. 22. System power output.

6. Conclusions

In operating the CHP, vast sources of energy required. To date, most of the CHP dryers use fuel energy for obtaining thermal energy to supplement the CHP. This is practically tedious, as it requires high maintenance and not so independently working. The SACHPD has come up with an improvement by adapting solar collector to supplement the CHP. This reduces the dependency of the drying technology on fossil energy for heating. The combination of chemical heat pump and solar technology gives extra efficiency in utilizing energy. The integration of solar thermal system to the CHP would assist in expanding the utilization of CHP also for many applications in the tropical region.

Acknowledgment

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